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## THE JOULE-THOMSON EFFECT IN AIR1

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Air compressed to a chosen pressure, lying between 30 and 220 atm., was passed through a temperature equalizing coil of pipe in an oil bath held at one of a series of temperatures between 25° and 300°C., around a resistance thermometer bulb, through the wall of a round ended tube of porous procelain, around a second thermometer inside the porcelain tube, through a control valve where it dropped to atmospheric pressure and finally back to the compressor. The oil-bath temperature was held constant by means of electrical heating controlled by an electrical thermostat. The inlet pressure was held exceedingly constant by a rotating piston barostat which controlled a spill valve through which a small fraction of the compressed air could be wasted. The steadiness of the inlet pressure is vital to such work and a large amount of experimental attention was spent toward attaining it. The temperature of the inlet thermometer and the difference of temperature between the two thermometers was read on a Callendar-Griffiths bridge. The flow of air was measured roughly by a Venturi meter.

The performance of this form of porous plug was studied in detail, particularly as depending on the external and internal arrangements. Theory demands that the difference of temperature across the wall should depend only on the temperature and pressure conditions, and not at all on the rate of flow or particular plug. All the data reported satisfied these conditions, except at the low pressure (large volume) state where kinetic energy effects were very difficult to control.

To obtain the maximum amount of information, the measurements were arranged in groups, in which the pressure dropped from the same initial

pressure successively to a series of values of the lower pressure, giving thus a corresponding series of lower temperatures. A plot of these readings, T against p, gave a curve along which (u + pv) remains constant—an isenthalpic curve. A group of such curves were obtained, one for each of the bath temperatures, 25, 50, 75, 100, 150, 200, 250, 283°C. In general, these curves show falling temperature with falling pressure, the latter being much greater at the lower temperatures and lower pressures.

The slope  $(\mu)$  of these curves, called the Joule-Thomson coefficient, was calculated by taking the ratio of successive differences of temperature to the respective successive differences of pressure. These values of  $\mu$  were plotted as a function of p and smooth curves (isenthalpics also) were drawn through them.

This data for  $\mu$  was next arranged as isopiestics by picking the values of  $\mu$  from the  $\mu$ , p plot for a group of integral values of p and the corresponding values of p from the original p, p curves. Table 1 was read off from the curves so obtained, and gives the values of  $\mu$  as a function of p and p.

TABLE 1

$\mu$ as a Function of $T$ and $p$									
PRES	s. 0°c.	25	50	75	100	150	200	250	280
1	0.2663	0.2269	0.1887	0.1581	0.1327	0.0927	0.0625	0.0402	0.0297
20	0.2494	0.2116	0.1777	0.1490	0.1244	0.0856	0.0564	0.0346	0.0246
6Ò	0.2143	0.1815	0.1527	0.1275	0.1057	0.0708	0.0447	0.0251	0.0161
100	0.1782	0.1517	0.1283	0.1073	0.0890	0.0587	0.0347	0.0164	0.0078
140	0.1445	0.1237	0.1047	0.0875	0.0723	0.0467	0.0258	0.0093	0.0011
180	0.1125	0.0974	0.0833	0.0800	0.0578	0.0366	0.0185	0.0027	-0.0054
220	0.0812	0.0718	0.0627	0.0542	0.0452	0.0286	0.0127	-0.0020	-0.0110

The data shows that the value of  $\mu$  falls steadily with rising temperature and with rising pressure till it goes through zero and becomes negative. The locus of  $\mu = 0$  was read from these curves and also measured by special experiments. Table 2 read from the plot gives its course over the range covered by the experiments.

TAI	BLE 2
P (ATM.)	T°C.
80	305
120	288
160	267
200	237

These values are widely different from previous experiments and calculations.

The temperature intercepts between the original isenthalpic curves can be used very directly to calculate the variation of specific heat  $(C_p)$  with pressure when  $C_p$  is known as a function of temperature. This latter was taken from the Reichsanstalt tables. The values so calculated are given in table 3.

TΑ	DI	E,	9	
10	.DI	æ	0	

C as a Function of $T$ and $p$										
PRESS.	0°c.	25	50	75	100	150	200	250	280	
1	0.2405	0.2410	0.2415	0.2419	0.2424	0.2434	0.2443	0.2453	0.2458	
20	0.2492	0.2487	0.2480	0.2475	0.2470	0.2466	0.2463	0.2468	0.2471	
60	0.2656	0.2627	0.2603	0.2581	0.2562	0.2532	0.2512	0.2500	0.2492	
100	0.2804	0.2760	0.2717	0.2681	0.2650	0.2602	0.2565	0.2536	0.2519	
140		0.2873	0.2816	0.2767	0.2725	0.2658	0.2607	0.2566	0.2544	
180		0.2960	0.2898	0.2840	0.2790	0.2707	0.2644	0.2596	0.2569	
220		0.3020	0.2956	0.2893	0.2838	0.2748	0.2678	0.2622	0.2593	

It will be observed that  $C_p$  increases with both pressure and temperature but at a decreasing rate.

The variation of  $C_p$  with pressure may be compared with the directly measured values. In table 4 the Reichsanstalt value for the average temperature 60°C. is given under  $C_{60}$ , and those of the present work under C, in both cases using the same value at 1 atm. as the starting point.

TABLE 4

COMPARISON OF C'S AT 60°C.							
PRESS.	1	20	60	100	140	180	220
Factor	1.0	1.025	1.0725	1.118	1.157	1.189	1.2125
C	0.2419	0.2480	0.2595	0.2705	0.2799	0.2876	0.2933
$C_{60}$	0.2419	0.2473	0.2590	0.2699	0.2805	0.2884	0.2950
Diff. %	0	+0.28	+0.19	-0.22	-0.21	-0.28	-0.59

The value of  $\mu$  may be used to calculate the correction to the air thermometer scale to reduce its readings to the thermodynamic scale. Using the available values for the coefficient of expansion between 0° and 100°C., leads to 273.15°K. as the temperature of the ice point on the thermodynamic scale.

The same general relation may be used to calculate the variation of this coefficient of expansion with pressure. In table 5 are given the values so calculated assuming the value at 1 atm. as given there. Under  $\alpha_1$  are Witkowski's directly measured data and under  $\alpha_2$  Holborn and Schulze's.

TABLE 5

Coefficient of Expansion									
Þ	<b>v</b> •	$I_p \times 10^5$	D	E%	$\alpha \times 10^{3}$	$a_1 \times 10^3$	$\alpha_2 \times 10^3$		
0	œ		1.0		3.6610				
1	773.4	4.725	1.0025	0.003	3.6704		3.666		
20	38.28	4.568	1.0503	0.05	3.845	3.83	3.826		
60	12.54	3.869	1.1300	0.1	4.137	4.18	4.166		
100	7.49	3.571	1.2009	0.2	4.397	4.41	4.424		

The values for  $\mu$  of the present paper are lower than Joule and Thomson's, and decidedly lower than Hoxton's. They are somewhat lower than Noell's, who covered about the same field but obtained very erratic data. This uncertainty may be attributed to lack of careful temperature

and pressure regulation as well as to very questionable thermal conditions about his plug.

The present work is to be extended as rapidly as possible to the region below room temperature.

<sup>1</sup> The full details will be found in Proc. Amer. Acad., Boston, 60, 537, 1925.

## ON NORMAL COÖRDINATES IN THE GEOMETRY OF PATHS

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1. It has been shown that in terms of the normal coördinates for the geometry of paths, the paths through the origin have linear equations and consequently are represented in an associated euclidean space by straight lines through the origin. It is well known that the paths are left unaltered by a change of the affine connection of the form

$$\Gamma_{ik}^{i} = \Gamma_{ik}^{\prime i} + \delta_{i}^{i} \varphi_{k} + \delta_{k}^{i} \varphi_{i} \tag{1.1}$$

where  $\varphi_j$  is an arbitrary vector.<sup>2</sup> Under such a change the ordinary normal coördinates are not invariant,<sup>3</sup> but undergo some transformation of the group which leaves invariant the straight lines through the origin of the associated euclidean space. Professor Veblen<sup>4</sup> in his presidential address to the American Mathematical Society remarked that this transformation would be linear fractional if the vector  $\varphi$  were properly chosen. In the present paper is found a necessary and sufficient condition that the transformation of normal coördinates corresponding to a change of affine connection (1.1) be linear fractional at every point. Two other conditions which are sufficient, but not necessary, are also given.

As by-products we obtain a set of identities (2.15) connecting the components of the rth extension of a covariant vector with those of the covariant derivative of its (r-1)th extension.

2. Let  $y^i$  be the normal coördinates associated with a point  $x^i = q^i$  and a coördinate system x. Let the corresponding equations of the paths be

$$\frac{d^2y^i}{ds^2} + C^i_{jk}\frac{dy^j}{ds}\frac{dy^k}{ds} = 0. (2.1)$$

If the affine connection be changed so that

$$C_{jk}^{\prime i} = C_{jk}^i - \delta_j^i \psi_k - \delta_k^i \psi_j,$$